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(54) LITHIUM-CONTAINING TRANSITION METAL MULTIPLE OXIDE AND MANUFACTURING METHOD THEREOF

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a positive electrode active material for a lithium secondary cell having a wide usable voltage range, the excellent durability against charge/ discharge cycle, high capacity and safety.

SOLUTION: The lithium-containing transition metal multiple oxide, in which the average number of valency of nickel-manganese-metal element M in a lithium-containing nickel-manganese-metal element M multiple oxide for a lithium secondary cell is 2.700-2.970, is used as the positive electrode active material for the lithium secondary cell. The lithium-containing nickel-manganese-metal element M multiple oxide for a lithium secondary cell is formed by firing a nickel-manganese-metal element M multiple compound and a lithium compound and is expressed by a general formula,  $\text{LiNixMn}_{1-x-y}\text{MyO}_2$  (where, (x) and (y) are respectively  $0.30 \leq x \leq 0.65$ ,  $0 \leq y \leq 0.2$  and M represent a metal element selected from Fe, Co, Cr, Al, Ti, Ga, In and Sn).

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**CLAIMS**

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**[Claim(s)]**

[Claim 1] General formula  $\text{LiNixMn}^{1-x-y}\text{MyO}_2$  (however, it is  $0.30 \leq x \leq 0.65$  and  $0 \leq y \leq 0.20$ .) M is a metallic element chosen from Fe, Co, Cr, aluminum, Ti, Ga, In, or Sn. Lithium content transition-metals multiple oxide for lithium secondary battery positive active material characterized by the average valences of the element which is expressed and consists of nickel, manganese, and a metallic element M being 2.700-2.970.

[Claim 2] The lithium content transition-metals multiple oxide according to claim 1 characterized by being R-3m rhombohedron structure, and specific surface area being below  $2\text{m}^2/\text{g}$ .

[Claim 3] The lithium content transition-metals multiple oxide according to claim 1 or 2 characterized by for the lattice constant of an a-axis being 2.895-2.925Å, and the lattice constant of a c-axis being 14.28-14.38Å.

[Claim 4] A lithium content transition-metals multiple oxide given in claim 1 characterized by exoergic initiation temperature being 255 degrees C or more thru/or any 1 term of 3.

[Claim 5] A lithium content transition-metals multiple oxide given in claim 1 characterized by fine-particles press consistencies being three or more 2.9 g/cm thru/or any 1 term of 4.

[Claim 6] The manufacture approach of the lithium content transition-metals multiple oxide characterized by being the approach of manufacturing the lithium content transition-metals multiple oxide of a publication in claim 1 thru/or any 1 term of 5, mixing a nickel-manganese-metallic element M coprecipitation conjugated compound and a lithium compound, and calcinating this mixture at 500-1000 degrees C in an inert atmosphere.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the improved lithium content transition-metals multiple oxide which is used as positive active material of a lithium secondary battery.

[0002]

[Description of the Prior Art] Small and the expectation for the nonaqueous electrolyte rechargeable battery which is lightweight and has a high energy consistency are growing as portable-izing of a device and cordless-ization progress in recent years. The multiple oxide of lithiums, such as  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiMn}_2\text{O}_4$ , and  $\text{LiMnO}_2$ , and transition metals is known by the active material for nonaqueous electrolyte rechargeable batteries.

[0003] In it, as a cheap ingredient with safety especially high recently and, research of the multiple oxide of a lithium and manganese is done briskly, these are used for positive active material, and development of the nonaqueous electrolyte rechargeable battery of the high voltage by combining negative-electrode active materials, such as occlusion and a carbon material which can be emitted, and a high energy consistency is furthered in the lithium.

[0004] Generally, the positive active material used for a nonaqueous electrolyte rechargeable battery becomes the lithium which is the main active material from the multiple oxide which made transition metals including cobalt, nickel, and manganese dissolve. With classes of the transition metals used, the electrode characteristics, such as electric capacity, reversibility, operating potential, and safety, change.

[0005] For example, the nonaqueous electrolyte rechargeable battery which used for positive active material  $\text{R-3m}$  rhombohedron rock salt stratified multiple oxide which made cobalt and nickel dissolve like  $\text{LiCoO}_2$  and  $\text{LiNi}_0.8\text{Co}_0.2\text{O}_2$  shows good reversibility in high electrical-potential-difference regions, such as 2.7-4.3V, while being able to attain 140 - 160 mAh/g and 180 - 200 mAh/g, and a comparatively high capacity consistency, respectively.

[0006]

[Problem(s) to be Solved by the Invention] However, when a cell is warmed, since the problem on which a cell tends to generate heat by the reaction of the positive active material at the time of charge and an electrolytic-solution solvent, the cobalt used as a raw material, and nickel are expensive, there is a problem to which the cost of an active material becomes high.

[0007] The proposal of  $\text{LiNi}_0.75\text{Co}_0.20\text{Mn}_0.05\text{O}_2$  is made by JP,10-027611,A that the property of  $\text{LiNi}_0.8\text{Co}_0.2\text{O}_2$  should be improved. Moreover, although the proposal is made by JP,10-81521,A about the manufacture approach of the nickel-manganese system hydroxide raw material for lithium cells of 2 yuan of having specific particle size distribution, in which thing, the positive active material which is satisfied with coincidence of three persons of charge-and-discharge capacity, cycle endurance, and safety is not obtained.

[0008] Moreover, the cell using  $\text{LiMnO}_2$  of a prismatic crystal Pmm system or a monoclinic system C2/m system,  $\text{LiMn}_0.95\text{Cr}_0.05\text{O}_2$ , or  $\text{LiMn}_0.9\text{aluminum}_0.1\text{O}_2$  has high safety, change of the crystal structure accompanying the charge-and-discharge cycle of a certain thing tends to take place, and the example which initial capacity discovers highly has the problem which becomes inadequate [ cycle endurance ].

[0009] Furthermore, although the proposal of  $\text{LiNixMn}_{1-x}\text{O}_2$  is made by each official report of JP,5-283076,A, JP,8-171910,A, JP,2000-294240,A, and JP,2000-223157,A and the proposal of  $\text{LiCobMncMdN}_{1-(b+c+d)}\text{O}_2$  is made by JP,11-25957,A, that with which all are satisfied of both capacity charge-and-discharge cycle

endurance and safety per capacity and volume per weight is not obtained.

[0010] Made in order that this invention might solve such a technical problem, the purpose has a high capacity and is to offer the positive-electrode ingredient for nonaqueous electrolyte rechargeable batteries of the Takayasu all nature excellent in charge-and-discharge cycle endurance.

[0011]

[Means for Solving the Problem] In order to attain the above-mentioned purpose, this invention is general formula  $\text{LiNixMn1-x-yMyO2}$  (however, it is  $0.30 \leq x \leq 0.65$  and  $0 \leq y \leq 0.20$ ). M is a metallic element chosen from Fe, Co, Cr, aluminum, Ti, Ga, In, or Sn. It is expressed and the lithium content transition-metals multiple oxide for lithium secondary battery positive active material (henceforth "the multiple oxide of this invention") characterized by the average valences of the element which consists of nickel, manganese, and a metallic element M being 2.700-2.970 is offered.

[0012] As a result of active oxygen's consisting is easy to be emitted of a positive electrode when a cell is charged if the above-mentioned average valence is larger than 2.970, since oxidation reaction of the electrolytic solution tends to progress and the safety of a cell falls, it is not desirable.

[0013] Moreover, when the above-mentioned average valence is larger than 2.970, crystal growth is late to lithiation reaction time, and since it becomes impossible to be filled up precisely [ when press molding of the active material is carried out ] as a result of growth of the aggregated particle by condensation of a crystal becoming slow, and the capacity per volume falls, or the specific surface area of active material powder becomes high and the dissolution to the electrolytic solution of manganese becomes easy to take place, it is not desirable.

[0014] In another side, if the above-mentioned average valence is smaller than 2.700, since the capacity per weight will fall, it is not desirable. In this invention, especially desirable average valences are 2.850-2.950.

[0015] Moreover, as for the specific surface area of the multiple oxide of this invention, it is desirable that it is below  $2\text{m}^2/\text{g}$ . If specific surface area exceeds  $2\text{m}^2/\text{g}$ , since cell capacity falls with time, in the so-called lithium ion battery of the rocking chair mold which it becomes easy to dissolve the manganese in a positive electrode in the electrolytic solution at the time of elevated-temperature use of a cell, and uses a carbon material especially for a negative electrode, it is not desirable. Below  $1\text{m}^2/\text{g}$  of especially specific surface area is desirable.

[0016] As for especially the multiple oxide of this invention, it is desirable that it is the active material which has R-3m rhombohedron structure from the field of charge-and-discharge cycle endurance. In this invention, it is still more desirable that the lattice constant of the a-axis in R-3m rhombohedron structure is 2.895-2.925Å, and the lattice constant of a c-axis is 14.28-14.38Å. Since the safety of a cell etc. will fall if a lattice constant separates from this range, it is not desirable.

[0017] Moreover, exoergic initiation temperature is 255 degrees C or more, and, as for the multiple oxide of this invention, this point is also mentioned to one of the descriptions of this invention. In this invention, when exoergic initiation temperature washes with a solvent the positive electrode charged at 50 degrees C 4.3V and it carries out a temperature up with ethylene carbonate by making a lithium into a counter electrode, it means the temperature by which a reaction with the electrolytic solution is started.

[0018] According to this invention, positive active material with high safety with exoergic initiation temperature specially high as mentioned above is offered. That is, to the exoergic initiation temperature of the conventional exoergic initiation temperature of  $\text{LiCoO}_2$  being around 175 degrees C as for a case of  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  before and behind 155 degrees C, and the exoergic initiation temperature of  $\text{LiMn}_2\text{O}_4$  being around 235 degrees C, since exoergic initiation temperature is as remarkable as 255 degrees C or more and the multiple oxide of this invention is expensive compared with them, the safety of a cell is raised.

[0019] According to this, it is desirable that they are three or more  $2.9\text{ g/cm}^3$ , and the fine-particles press consistency of the multiple oxide of this invention mixes a binder and a solvent to active material powder, makes them with a slurry, and coating and desiccation, and when it presses, it can make capacity per volume high at charge collector aluminum foil. Especially desirable fine-particles press consistencies are three or more  $3.1\text{ g/cm}^3$ .

[0020] The fine-particles press consistency in this invention means the apparent density gravity which calculated powder from the volume and weight of a molding object when carrying out a hydraulic press by the pressure of  $1\text{ t/cm}^2$ . the positive active material by this invention -- the conventional manganese spinel  $\text{LiMn}_2\text{O}_4$  and a lithium stratified manganese compound, for example, the fine-particles press consistency of

$\text{LiMnO}_2$ , -- at most -- compared with being about  $2.6 \text{ g/cm}^3$ , since the fine-particles press consistency is as high as several steps, it also has the description which can make the capacity consistency per volume of a cell remarkably higher than old lithium-manganic acid ghost positive active material.

[0021] In above-mentioned general formula  $\text{LiNi}_x\text{Mn}_{1-x-y}\text{MyO}_2$ , since it is it hard coming to take stable R-3m rhombohedron structure that  $x$  is less than 0.30, it is not desirable. Moreover, if  $x$  exceeds 0.65, since safety will fall, it is not desirable. Especially the desirable range of  $x$  is 0.40-0.55.

[0022] Since that it is one metallic element atom of Fe, Co, Cr, aluminum, Ti, Ga, In, and Sn can aim at improvement in charge-and-discharge cycle endurance, safety, capacity, etc., a metallic element M is desirable. the addition  $y$  of M atom --  $0 \leq y \leq 0.20$  -- it is -- desirable -- 0.01 to 0.18 -- it is 0.05-0.16 especially preferably.

[0023] Moreover, in manufacturing the above-mentioned lithium content transition-metals multiple oxide for lithium secondary battery positive active material, this invention mixes a nickel-manganese-metallic element M coprecipitation conjugated compound and a lithium compound, and is characterized by calcinating this mixture at 500-1000 degrees C in an inert atmosphere. As a lithium compound used for a reaction, a lithium hydroxide, a lithium carbonate, and lithium oxide are illustrated preferably.

[0024] As a nickel-manganese-metallic element M coprecipitation conjugated compound A nickel-manganese-metallic element M salt water solution, an alkali-metal hydroxy compound, and an ammonium ion supply object are supplied to the system of reaction respectively continuously or intermittently. Where it made temperature of the system of reaction into the constant temperature within the limits of 30-70 degrees C and pH is held to the constant value of 10-13 within the limits, a reaction is advanced, and it is general formula  $\text{Ni}_x\text{Mn}_{1-x-y}\text{My}(\text{OH})_p$  (however, it is  $0.30 \leq x \leq 0.65$ ,  $0 \leq y \leq 0.20$ , and  $2 \leq p \leq 4$ ). M is chosen from Fe, Co, Cr, aluminum, Ti, Ga, In, or Sn. The nickel-manganese-metallic element M coprecipitation compound hydroxide which has the almost spherical particle shape which is made to \*\*\*\* the nickel-manganese-metallic element M coprecipitation compound hydroxide expressed, and is acquired, Or the nickel-manganese-metallic element M coprecipitation compound oxy-hydroxide which an oxidizer is made to act on the above-mentioned nickel-manganese-metallic element M coprecipitation compound hydroxide, and is obtained, Or it is desirable that it is especially either of the nickel-manganese-metallic element M coprecipitation multiple oxides which calcinate the above-mentioned nickel-manganese-metallic element M coprecipitation compound hydroxide or the above-mentioned nickel-manganese-metallic element M coprecipitation compound oxy-hydroxide, and are obtained.

[0025]

[Embodiment of the Invention] The multiple oxide of this invention is obtained by calcinating the mixture of the nickel-manganese-metallic element M coprecipitation compound powder chosen from for example, a nickel-manganese-metallic element M coprecipitation compound hydroxide, a nickel-manganese-metallic element M coprecipitation compound oxy-hydroxide, or a nickel-manganese-metallic element M coprecipitation multiple oxide, and lithium compound powder (preferably a lithium hydroxide, a lithium carbonate, lithium oxide) at 500-1000 degrees C of solid phase techniques under an inert gas ambient atmosphere for 5 to 40 hours.

[0026] A temperature requirement is 750-950 degrees C especially preferably. Moreover, if it calcinates in an oxygen content ambient atmosphere, for example, atmospheric air, since the average valence of the desired manganese-nickel-metallic element M will become high, it is not desirable. As long as the average valences 2.70-2.97 of the manganese-nickel-metallic element M specified to this invention are obtained, low-concentration oxygen may be contained in inert gas. Although this permission oxygen density is dependent also on burning temperature and an active material presentation, 1000 ppm or less, 10 etc. ppm or less, etc. are adopted suitably 1% or less, for example.

[0027] mixing carbon system electric conduction material and binding material, such as acetylene black, a graphite, and ketch en black, to the powder of the multiple oxide of this invention -- a positive electrode -- a mixture is formed. Polyvinylidene fluoride, polytetrafluoroethylene, a polyamide, a carboxymethyl cellulose, acrylic resin, etc. are used for binding material. the slurry which consists of the solvent or dispersion medium of the powder of the multiple oxide of this invention, electric conduction material, binding material, and binding material -- positive-electrode charge collectors, such as aluminium foil, -- coating - it dries and rolls [ press ] out and a positive-active-material layer is formed on a positive-electrode charge collector.

[0028] In the lithium cell using the multiple oxide of this invention as positive active material, a carbonate is

desirable as a solvent of an electrolytic solution. a carbonate -- the shape of annular and a chain -- all can be used. Propylene carbonate, ethylene carbonate, etc. are illustrated as an annular carbonate. As a chain-like carbonate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, methylpropyl carbonate, methyl isopropyl carbonate, etc. are illustrated.

[0029] It may be independent, or the above-mentioned carbonate may be used for two or more sorts, mixing. Moreover, you may use it, mixing with other solvents. Moreover, if a chain-like carbonate and an annular carbonate are used together depending on the ingredient of a negative-electrode active material, a discharge property, cycle endurance, and charge-and-discharge effectiveness may be improvable. Moreover, it is good also as a gel polymer electrolyte by adding a vinylidene fluoride-hexafluoropropylene copolymer (for example, Atochem KAINA) and a vinylidene fluoride-perfluoro propyl vinyl ether copolymer to these organic solvents, and adding the following solute.

[0030] It is desirable to use as a solute any one or more sorts of the lithium salt which makes an anion  $\text{ClO}_4^-$ ,  $\text{CF}_3\text{SO}_3^-$ ,  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $\text{AsF}_6^-$ ,  $\text{SbF}_6^-$ ,  $\text{CF}_3\text{CO}_2^-$ ,  $2(\text{CF}_3\text{SO}_2)\text{N}^-$ , etc. As for an above-mentioned electrolytic solution or an above-mentioned polymer electrolyte, it is desirable to add the electrolyte which consists of lithium salt by the concentration of 0.2-2.0 mols / L to the above-mentioned solvent or a solvent content polymer. If it deviates from this range, ionic conductivity will fall and electrolytic electrical conductivity will fall. 0.5 - 1.5 mol/L is selected more preferably. Porosity polyethylene and a porosity polypropylene film are used for a separator.

[0031] The ingredient which emits [ occlusion and ] a lithium ion is used for a negative-electrode active material. Although especially the ingredient that forms a negative-electrode active material is not limited, a lithium metal, a lithium alloy, a carbon material, a periodic table 14, the oxide that made 15 groups' metal the subject, a carbon compound, a silicon carbide compound, a silicon oxide compound, a titanium sulfide, a boron carbide compound, etc. are mentioned, for example.

[0032] What pyrolyzed the organic substance on various pyrolysis conditions as a carbon material, an artificial graphite, a natural graphite, a soil graphite, expanded graphite, a scale-like graphite, etc. can be used. Moreover, the compound which makes the tin oxide a subject can be used as an oxide. Copper foil, a nickel foil, etc. are used as a negative-electrode charge collector.

[0033] As for a positive electrode and a negative electrode, it is desirable to knead an active material with an organic solvent, to consider as a slurry, to apply, dry and press this slurry in a metallic foil charge collector, and to obtain it to it. There is especially no constraint in the configuration of the lithium cell using the multiple oxide of this invention. The shape of a sheet (the shape of so-called film), the letter of folding, a winding mold closed-end cylindrical shape, a carbon button form, etc. are chosen according to an application.

[0034]

[Example] Next, although the concrete examples 1-9 and the examples 1-3 of a comparison of this invention are explained, this invention is not limited to these examples.

[0035] <<example 1>> The metal sulfate water solution containing a nickel sulfate and a manganese sulfate, the aqueous ammonia solution, and the caustic-alkali-of-sodium water solution were continuously supplied so that pH in a reaction vessel might be set to 11.35. Temperature was held at 50 degrees C. After the reaction, the slurry was rinsed [ filtration ] and dried, it was spherical and nickel-manganese coprecipitation hydroxide fine particles with a mean particle diameter of 8 micrometers were obtained. These nickel-manganese coprecipitation hydroxide fine particles were calcinated and ground in atmospheric air at 550 degrees C, and nickel-manganese coprecipitation oxide powder was obtained. This nickel-manganese coprecipitation oxide powder and lithium-hydroxide powder were mixed, it calcinated and ground at 830 degrees C among nitrogen-gas-atmosphere mind, and  $\text{LiNi}_0.50\text{Mn}_0.50\text{O}_2$  with a mean particle diameter of 7 micrometers was compounded. X-ray diffraction analysis by  $\text{CuK}\alpha$  of this powder showed that it was R-3m rhombohedron stratified rock salt type structure. By lied belt analysis, the lattice constant of 2.902Å and a c-axis of the lattice constant of an a-axis was 14.32Å. Moreover, it was 2.917 when it asked for the average valence of nickel and manganese about this powder with the oxidation reduction titration and the chelatometry which used  $\text{FeSO}_4$  and  $\text{KMnO}_4$ . The specific surface area of this powder was 0.78m<sup>2</sup>/g. When the hydraulic press of the 1t /of the  $0.50\text{LiNi}_0.50\text{Mn}_2$  obtained powder was carried out by the pressure of 2 cm and the fine-particles press consistency was calculated from the volume and weight, it was 3.15 g/cm<sup>3</sup>. Ball mill mixing of this  $\text{LiNi}_0.50\text{Mn}_0.50\text{O}_2$  powder, and acetylene black and polyvinylidene fluoride was carried out adding

N-methyl pyrrolidone by the weight ratio of 83/10/7, and it considered as the slurry. This slurry was applied on the aluminium foil positive-electrode charge collector with a thickness of 20 micrometers, it dried at 150 degrees C, and N-methyl pyrrolidone was removed. Roll press rolling was carried out to after an appropriate time, and the positive-electrode object was acquired. A metal lithium foil with a thickness of 300 micrometers is used for a separator at a negative electrode using porosity polyethylene with a thickness of 25 micrometers, a nickel foil is used for a negative-electrode charge collector, and it is 1M in the electrolytic solution. The coin cell 2030 mold was assembled in the argon glove compartment using LiPF<sub>6</sub>/EC+DEC (1:1). And under the 60-degree C temperature ambient atmosphere, constant-current charge was carried out to 4.3V by 30mA per 1g of positive active material, constant-current discharge was carried out to 2.7V in 30mA per 1g of positive active material, the charge-and-discharge cycle trial was performed 30 times, and it asked for the capacity maintenance factor from the ratio of the discharge capacity after 2 times charge and discharge, and the discharge capacity after 30 times charge and discharge. Moreover, the short form sealing cel was assembled in the argon glove compartment using the same positive electrode and the same separator, a negative electrode, and the electrolytic solution for cell safety evaluation. After charging this short form cel to 4.3V under a 50-degree C temperature ambient atmosphere, the cel was disassembled under the room temperature, and exoergic initiation temperature in case the positive electrode was put into the well-closed container and carries out a temperature up to a sample using nothing and differential-scanning-calorimetry equipment with ethylene carbonate was searched for. Initial capacity was [ the exoergic initiation temperature of 149 mAh/g and a capacity maintenance factor ] 283 degrees C 92%.

[0036] <<example 2>> The metal sulfate water solution containing a nickel sulfate, a manganese sulfate, and cobalt sulfate was used as a metal sulfate water solution, and also nickel-manganese-cobalt coprecipitation hydroxide fine particles of 8 micrometers of mean diameters were obtained like the above-mentioned example 1. These nickel-manganese-cobalt coprecipitation hydroxide fine particles were calcinated and ground in atmospheric air at 550 degrees C, and nickel-manganese-cobalt coprecipitation oxide powder was obtained. This nickel-manganese-cobalt coprecipitation oxide powder and lithium-hydroxide powder were mixed, it calcinated and ground at 830 degrees C among nitrogen-gas-atmosphere mind, and LiNi<sub>0.45</sub>Mn<sub>0.45</sub>Co<sub>0.10</sub>O<sub>2</sub> with a mean particle diameter of 6 micrometers was compounded. X-ray diffraction analysis by CuKalpha of this powder showed that it was R-3m rhombohedron stratified rock salt type structure. By lied belt analysis, the lattice constant of 2.903A and a c-axis of the lattice constant of an a-axis was 14.34A. Moreover, it was 2.873 when it asked for the average valence of nickel, manganese, and cobalt like the above-mentioned example 1 about this powder. The specific surface area of this powder was 0.79m<sup>2</sup>/g. The fine-particles press consistencies were 3.08 g/cm<sup>3</sup>. LiNi<sub>0.45</sub>Mn<sub>0.45</sub>Co<sub>0.10</sub>O<sub>2</sub> was used instead of LiNi<sub>0.50</sub>Mn<sub>0.50</sub>O<sub>2</sub> of the above-mentioned example 1, and also the positive-electrode object and the cell were produced like the above-mentioned example 1, and the property was evaluated. Initial capacity was [ the exoergic initiation temperature of 155 mAh/g and a capacity maintenance factor ] 275 degrees C 96%.

[0037] <<example 3>> The aluminum sulfate was used instead of the cobalt sulfate in the metal sulfate water solution of the above-mentioned example 2, and also nickel-manganese-aluminum coprecipitation oxide was compounded like the above-mentioned example 2, and, subsequently the lithium-nickel-manganese-aluminum multiple oxide powder (LiNi<sub>0.45</sub>Mn<sub>0.45</sub>aluminum<sub>0.10</sub>O<sub>2</sub>) of 5 micrometers of mean diameters was compounded like the above-mentioned example 1. X-ray diffraction analysis by CuKalpha of this powder showed that it was R-3m rhombohedron stratified rock salt type structure. By lied belt analysis, the lattice constant of 2.896A and a c-axis of the lattice constant of an a-axis was 14.29A. Moreover, it was 2.923 when it asked for the average valence of nickel, manganese, and cobalt like the above-mentioned example 1 about this powder. The specific surface area of this powder was 0.85m<sup>2</sup>/g. The fine-particles press consistencies were 3.07 g/cm<sup>3</sup>. LiNi<sub>0.45</sub>Mn<sub>0.45</sub>aluminum<sub>0.10</sub>O<sub>2</sub> was used instead of LiNi<sub>0.50</sub>Mn<sub>0.50</sub>O<sub>2</sub> of the above-mentioned example 1, and also the positive-electrode object and the cell were produced like the above-mentioned example 1, and the property was evaluated. Initial capacity was [ the exoergic initiation temperature of 150 mAh/g and a capacity maintenance factor ] 286 degrees C 94%.

[0038] <<example 4>> The iron sulfate was used instead of the cobalt sulfate in the metal sulfate water solution of the above-mentioned example 2, and also nickel-manganese-iron coprecipitation oxide was compounded like the above-mentioned example 2, and, subsequently the lithium-nickel-manganese-iron multiple oxide powder (LiNi<sub>0.45</sub>Mn<sub>0.45</sub>Fe<sub>0.10</sub>O<sub>2</sub>) of 5 micrometers of mean diameters was compounded like the above-mentioned



example 1. X-ray diffraction analysis by CuKalpha of this powder showed that it was R-3m rhombohedron stratified rock salt type structure. By lied belt analysis, the lattice constant of 2.901A and a c-axis of the lattice constant of an a-axis was 14.33A. Moreover, it was 2.927 when it asked for the average valence of nickel, manganese, and cobalt like the above-mentioned example 1 about this powder. The specific surface area of this powder was 0.83m<sup>2</sup>/g. The fine-particles press consistencies were 3.05 g/cm<sup>3</sup>. LiNi<sub>0.45</sub>Mn<sub>0.45</sub>Fe<sub>0.10</sub>O<sub>2</sub> was used instead of LiNi<sub>0.50</sub>Mn<sub>0.50</sub>O<sub>2</sub> of the above-mentioned example 1, and also the positive-electrode object and the cell were produced like the above-mentioned example 1, and the property was evaluated. Initial capacity was [ the exoergic initiation temperature of 151 mAh/g and a capacity maintenance factor ] 280 degrees C 94%.

[0039] <<example 5>> Sulfuric-acid titanium was used instead of the cobalt sulfate in the metal sulfate water solution of the above-mentioned example 2, and also the nickel-manganese-titanium coprecipitation hydroxide was compounded like the above-mentioned example 2, and, subsequently the lithium-nickel-manganese-titanium multiple oxide powder (LiNi<sub>0.45</sub>Mn<sub>0.45</sub>Ti<sub>0.10</sub>O<sub>2</sub>) of 5 micrometers of mean diameters was compounded like the above-mentioned example 1. X-ray diffraction analysis by CuKalpha of this powder showed that it was R-3m rhombohedron stratified rock salt type structure. By lied belt analysis, the lattice constant of 2.904A and a c-axis of the lattice constant of an a-axis was 14.34A. Moreover, it was 2.918 when it asked for the average valence of nickel, manganese, and cobalt like the above-mentioned example 1 about this powder. The specific surface area of this powder was 0.75m<sup>2</sup>/g. The fine-particles press consistencies were 3.11 g/cm<sup>3</sup>. LiNi<sub>0.45</sub>Mn<sub>0.45</sub>Ti<sub>0.10</sub>O<sub>2</sub> was used instead of LiNi<sub>0.50</sub>Mn<sub>0.50</sub>O<sub>2</sub> of the above-mentioned example 1, and also the positive-electrode object and the cell were produced like the above-mentioned example 1, and the property was evaluated. Initial capacity was [ the exoergic initiation temperature of 151 mAh/g and a capacity maintenance factor ] 285 degrees C 94%.

[0040] <<example 6>> The chromium sulfate was used instead of the cobalt sulfate in the metal sulfate water solution of the above-mentioned example 2, and also the nickel-manganese-chromium coprecipitation hydroxide was compounded like the above-mentioned example 2, and, subsequently the lithium-nickel-manganese-chromium multiple oxide powder (LiNi<sub>0.45</sub>Mn<sub>0.45</sub>Cr<sub>0.10</sub>O<sub>2</sub>) of 5 micrometers of mean diameters was compounded like the above-mentioned example 1. X-ray diffraction analysis by CuKalpha of this powder showed that it was R-3m rhombohedron stratified rock salt type structure. By lied belt analysis, the lattice constant of 2.902A and a c-axis of the lattice constant of an a-axis was 14.32A. Moreover, it was 2.920 when it asked for the average valence of nickel, manganese, and cobalt like the above-mentioned example 1 about this powder. The specific surface area of this powder was 0.79m<sup>2</sup>/g. The fine-particles press consistencies were 3.14 g/cm<sup>3</sup>. LiNi<sub>0.45</sub>Mn<sub>0.45</sub>Cr<sub>0.10</sub>O<sub>2</sub> was used instead of LiNi<sub>0.50</sub>Mn<sub>0.50</sub>O<sub>2</sub> of the above-mentioned example 1, and also the positive-electrode object and the cell were produced like the above-mentioned example 1, and the property was evaluated. Initial capacity was [ the exoergic initiation temperature of 153 mAh/g and a capacity maintenance factor ] 288 degrees C 94%.

[0041] <<example 7>> The sulfuric-acid gallium was used instead of the cobalt sulfate in the metal sulfate water solution of the above-mentioned example 2, and also the nickel-manganese-gallium coprecipitation hydroxide was compounded like the above-mentioned example 2, and, subsequently the lithium-manganese-gallium multiple oxide powder (LiNi<sub>0.45</sub>Mn<sub>0.45</sub>Ga<sub>0.10</sub>O<sub>2</sub>) of 5 micrometers of mean diameters was compounded like the above-mentioned example 1. X-ray diffraction analysis by CuKalpha of this powder showed that it was R-3m rhombohedron stratified rock salt type structure. By lied belt analysis, the lattice constant of 2.899A and a c-axis of the lattice constant of an a-axis was 14.30A. Moreover, it was 2.923 when it asked for the average valence of nickel, manganese, and cobalt like the above-mentioned example 1 about this powder. The specific surface area of this powder was 0.75m<sup>2</sup>/g. The fine-particles press consistencies were 3.06 g/cm<sup>3</sup>. LiNi<sub>0.45</sub>Mn<sub>0.45</sub>Ga<sub>0.10</sub>O<sub>2</sub> was used instead of LiNi<sub>0.50</sub>Mn<sub>0.50</sub>O<sub>2</sub> of the above-mentioned example 1, and also the positive-electrode object and the cell were produced like the above-mentioned example 1, and the property was evaluated. Initial capacity was [ the exoergic initiation temperature of 150 mAh/g and a capacity maintenance factor ] 281 degrees C 93%.

[0042] <<example 8>> Indium sulfate was used instead of the cobalt sulfate in the metal sulfate water solution of the above-mentioned example 2, and also nickel-manganese-indium coprecipitation oxide was compounded like the above-mentioned example 2, and, subsequently the lithium-manganese-indium multiple oxide powder (LiNi<sub>0.45</sub>Mn<sub>0.45</sub>In<sub>0.10</sub>O<sub>2</sub>) of 5 micrometers of mean diameters was compounded like the above-mentioned

example 1. X-ray diffraction analysis by CuKalpha of this powder showed that it was R-3m rhombohedron stratified rock salt type structure. By lied belt analysis, the lattice constant of 2.922A and a c-axis of the lattice constant of an a-axis was 14.36A. Moreover, it was 2.932 when it asked for the average valence of nickel, manganese, and cobalt like the above-mentioned example 1 about this powder. The specific surface area of this powder was 0.71m<sup>2</sup>/g. The fine-particles press consistencies were 3.13 g/cm<sup>3</sup>. LiNi<sub>0.45</sub>Mn<sub>0.45</sub>In<sub>0.10</sub>O<sub>2</sub> was used instead of LiNi<sub>0.50</sub>Mn<sub>0.50</sub>O<sub>2</sub> of the above-mentioned example 1, and also the positive-electrode object and the cell were produced like the above-mentioned example 1, and the property was evaluated. Initial capacity was [ the exoergic initiation temperature of 155 mAh/g and a capacity maintenance factor ] 282 degrees C 95%.

[0043] <<example 9>> Sulfuric-acid tin was used instead of the cobalt sulfate in the metal sulfate water solution of the above-mentioned example 2, and also nickel-manganese-tin coprecipitation oxide was compounded like the above-mentioned example 2, and, subsequently the lithium-manganese-tin multiple oxide powder (LiNi<sub>0.45</sub>Mn<sub>0.45</sub>Sn<sub>0.10</sub>O<sub>2</sub>) of 5 micrometers of mean diameters was compounded like the above-mentioned example 1. X-ray diffraction analysis by CuKalpha of this powder showed that it was R-3m rhombohedron stratified rock salt type structure. By lied belt analysis, the lattice constant of 2.910A and a c-axis of the lattice constant of an a-axis was 14.35A. Moreover, it was 2.900 when it asked for the average valence of nickel, manganese, and cobalt like the example 1 about this powder. The specific surface area of this powder was 0.85m<sup>2</sup>/g. The fine-particles press consistencies were 3.10 g/cm<sup>3</sup>. LiNi<sub>0.45</sub>Mn<sub>0.45</sub>Sn<sub>0.10</sub>O<sub>2</sub> was used instead of LiNi<sub>0.50</sub>Mn<sub>0.50</sub>O<sub>2</sub> of the above-mentioned example 1, and also the positive-electrode object and the cell were produced like the above-mentioned example 1, and the property was evaluated. Initial capacity was [ the exoergic initiation temperature of 152 mAh/g and a capacity maintenance factor ] 284 degrees C 94%.

[0044] <Example 1 of a comparison> Nickel-manganese coprecipitation oxide was compounded like the above-mentioned example 1, subsequently this nickel-manganese coprecipitation oxide powder and lithium-hydroxide powder were mixed, 8-hour baking and grinding of were done at 830 degrees C among atmospheric air, and LiNi<sub>0.50</sub>Mn<sub>0.50</sub>O<sub>2</sub> with a mean particle diameter of 7 micrometers was compounded. X-ray diffraction analysis by CuKalpha of this powder showed that it was R-3m rhombohedron stratified rock salt type structure. By lied belt analysis, the lattice constant of 2.888A and a c-axis of the lattice constant of an a-axis was 14.32A. Moreover, it was 2.997 when it asked for the average valence of nickel and manganese like the above-mentioned example 1 about this powder. The specific surface area of this powder was 9.62m<sup>2</sup>/g. The fine-particles press consistencies were 2.42 g/cm<sup>3</sup>. it was obtained by baking among atmospheric air instead of LiNi<sub>0.50</sub>Mn<sub>0.50</sub>O<sub>2</sub> of the above-mentioned example 1 -- this -- it was used LiNi<sub>0.50</sub>Mn<sub>0.50</sub>O<sub>2</sub>, and also the positive-electrode object and the cell were produced like the above-mentioned example 1, and the property was evaluated. Initial capacity was [ the exoergic initiation temperature of 149 mAh/g and a capacity maintenance factor ] 238 degrees C 92%.

[0045] <Example 2 of a comparison> Nickel-manganese-cobalt coprecipitation oxide was compounded like the above-mentioned example 2, subsequently this nickel-manganese coprecipitation oxide powder and lithium-hydroxide powder were mixed, 8-hour baking and grinding of were done at 830 degrees C among atmospheric air, and LiNi<sub>0.45</sub>Mn<sub>0.45</sub>Co<sub>0.10</sub>O<sub>2</sub> with a mean particle diameter of 7 micrometers was compounded. X-ray diffraction analysis by CuKalpha of this powder showed that it was R-3m rhombohedron stratified rock salt type structure. By lied belt analysis, the lattice constant of 2.885A and a c-axis of the lattice constant of an a-axis was 14.31A. Moreover, it was 2.986 when it asked for the average valence of nickel and manganese like the above-mentioned example 1 about this powder. The specific surface area of this powder was 9.89m<sup>2</sup>/g. The fine-particles press consistencies were 2.41 g/cm<sup>3</sup>. This LiNi<sub>0.45</sub>Mn<sub>0.45</sub>Co<sub>0.10</sub>O<sub>2</sub> obtained by baking among atmospheric air instead of LiNi<sub>0.50</sub>Mn<sub>0.50</sub>O<sub>2</sub> of the above-mentioned example 1 was used, and also the positive-electrode object and the cell were produced like the above-mentioned example 1, and the property was evaluated. Initial capacity was [ the exoergic initiation temperature of 153 mAh/g and a capacity maintenance factor ] 229 degrees C 95%.

[0046] <Example 3 of a comparison> The nickel sulfate in the metal sulfate water solution of the above-mentioned example 2 and the concentration of a manganese sulfate were changed, nickel-manganese-cobalt coprecipitation oxide was compounded like the above-mentioned example 2, and, subsequently the lithium-nickel-manganese-cobalt multiple oxide powder (LiNi<sub>0.70</sub>Mn<sub>0.20</sub>Co<sub>0.10</sub>O<sub>2</sub>) of 5 micrometers of mean

diameters was compounded by baking among atmospheric air like the above-mentioned example 2 of a comparison. X-ray diffraction analysis by CuKalpha of this powder showed that it was R-3m rhombohedron stratified rock salt type structure. Moreover, it was 3.002 when it asked for the average valence of nickel and manganese like the above-mentioned example 1 about this powder. The specific surface area of this powder was 1.26m<sup>2</sup>/g. It was used LiNi<sub>0.70</sub>Mn<sub>0.20</sub>Co<sub>0.10</sub>O<sub>2</sub> instead of LiNi<sub>0.50</sub>Mn<sub>0.50</sub>O<sub>2</sub> of the above-mentioned example 1, and also the positive-electrode object and the cell were produced like the above-mentioned example 1, and the property was evaluated. Initial capacity was [ the exoergic initiation temperature of 180 mAh/g and a capacity maintenance factor ] 181 degrees C 87%.

[0047] By reference, the result of the above-mentioned examples 1-9 and the examples 1-3 of a comparison is collectively shown in degree table.

[Table 1]

	a軸の格子定数 (Å)	c軸の格子定数 (Å)	平均粒径	比表面積 m <sup>2</sup> /g	密度プレス密度 g/cm <sup>3</sup>	初期容量 (mAh/g)	容量維持率 (%)	充放電温度 (°C)
実施例 1	2.902	14.32	2.917	0.78	3.15	149	92	283
実施例 2	2.903	14.34	2.873	0.79	3.08	155	96	275
実施例 3	2.896	14.29	2.923	0.85	3.07	150	94	286
実施例 4	2.901	14.33	2.927	0.83	3.05	151	94	280
実施例 5	2.904	14.34	2.918	0.75	3.11	151	94	285
実施例 6	2.902	14.32	2.920	0.79	3.14	153	94	288
実施例 7	2.899	14.30	2.923	0.75	3.06	150	93	281
実施例 8	2.922	14.36	2.932	0.71	3.13	155	95	282
実施例 9	2.910	14.35	2.900	0.85	3.10	152	94	284
比較例 1	2.888	14.32	2.997	9.62	2.42	149	92	238
比較例 2	2.885	14.31	2.986	9.89	2.41	153	95	229
比較例 3	—	—	3.002	1.26	—	180	87	181

[0048]

[Effect of the Invention] While the usable electrical-potential-difference range is wide and charge-and-discharge cycle endurance is good by using the lithium content nickel-manganese-metallic element M multiple oxide of this invention as positive active material of a lithium secondary battery, a cell with high safety with a high and capacity is obtained.

[Translation done.]